

PATENT SPECIFICATION



Convention Date (United States of America): Dec. 26, 194 - 573,642

Application Date (In United Kingdom): Dec. 14, 1943. No. 20976/43.

Complete Specification Accepted: Nov. 29, 1945.

COMPLETE SPECIFICATION

Extraction of Hydracrylic Acid

We, AMERICAN CYANAMID COMPANY, a corporation organized under the laws of the State of Maine, United States of America, of 30, Rockefeller Plaza, New York, New York, United States of America, (Assignees of BRYAN COLLINS REDMON and GEORGE ROBERT GRIFFIN, both citizens of the United States of America, respectively, of Trinity Pass, Stamford, and Catoon Lane, Stamford, Connecticut, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

This invention relates to the extraction of hydracrylic acid from aqueous solutions containing a salt or from a salt cake.

Hydracrylic acid may be prepared conveniently by the alkaline hydrolysis of ethylene cyanohydrin followed by treatment with a mineral acid such as sulphuric acid. The resulting solution contains free hydracrylic acid, minor proportions of impurities such as amine compounds and a salt such as sodium sulphate.

An object of this invention is to provide a process for extracting hydracrylic acid from a salt.

Another object of our invention is to provide a method of separating hydracrylic acid from a salt and from impurities formed in the preparation of hydracrylic acid from ethylene cyanohydrin.

These and other objects are attained by extracting hydracrylic acid from a mixture with a salt or from a solution containing a salt by means of a ketone having no more than a total of six carbon atoms and preferably those which boil below 100° C.

The following examples in which the proportions are in parts by weight are given by way of illustration and not in limitation.

EXAMPLE 1:

Ethylene cyanohydrin	710 parts
Sodium hydroxide	400 "
Water	1000 "
Sulphuric acid (95.5%)	513 "
Acetone	2380 "

[Price 1/-]

The ethylene cyanohydrin is added to a solution of the sodium hydroxide in the water slowly and either continuously or in small proportions over a period of about 1 hour. The reacting mixture is maintained at a temperature of 95°—100° C. during the addition of the ethylene cyanohydrin and it is agitated by any convenient means.

A large proportion of ammonia which is liberated during the addition of the ethylene cyanohydrin is given off and its removal may be facilitated by introducing a small stream of air or steam into the reacting mixture. After all of the ethylene cyanohydrin is added, the solution may be maintained at the reaction temperature for from a few minutes to an hour or more in order to insure the complete hydrolysis of any unreacted ethylene cyanohydrin. The residual ammonia may be volatilized from the solution and part of the water may be removed, thereby providing a solution of sodium hydracrylate. The solution may be advantageously evaporated to the point where solid material begins to precipitate from the hot solution. It is desirable that the ammonia set free by the hydrolysis of the ethylene cyanohydrin be completely removed.

The solution of sodium hydracrylate prepared in accordance with the foregoing description is cooled to about 40° C. after which the sulphuric acid is added. During the addition of the acid the temperature of the solution is maintained at about 35°—50° C. Substantially all water is then removed from the solution by heating under about 30 mm. of mercury absolute pressure and with constant evaporation. A small proportion of the acetone may be mixed with the resulting slurry and the precipitated sodium sulphate is filtered from the hydracrylic acid and the acetone. The sodium sulphate filter cake is extracted continuously or by decantation with the acetone.

One method for carrying out a continuous extraction of the salt cake is to pass the acetone through the filter in which the salt cake has been collected, thence to a receiver which is heated by

any suitable means in order to volatilize the solvent which then passes to a condenser and finally back through the filter containing the salt cake. The solvent extracting process may be carried out from one to several hours or more. The original filtrate and the acetone containing the hydracrylic acid are combined and filtered to remove any trace of residual sodium sulphate. The acetone is removed from the combined solution by evaporation at atmospheric pressure, followed by evaporation at about 20—30 mm. of mercury absolute pressure. The product is substantially pure hydracrylic acid and it is an amber coloured viscous liquid. A yield of about 85%—95% of the theoretical is obtained.

EXAMPLE 2.

Ethylene cyanohydrin	710 parts
Sodium hydroxide	400 "
Water	1000 "
Sulphuric acid (95.5%)	518 "
Methyl ethyl ketone	1610 "

The ethylene cyanohydrin is reacted with the sodium hydroxide in the water and the resulting sodium hydracrylate is converted into the hydracrylic acid in the same manner as that described in Example 1.

The solution containing the hydracrylic acid and sodium sulphate is filtered and extracted with the methyl ethyl ketone as described in Example 1. A yield of about 92% of hydracrylic acid is obtained.

The solution containing hydracrylic acid which is obtained upon adding the sulphuric acid in the Example 1 and 2 may be extracted with a ketone without evaporation and filtration or with only partial evaporation. However, it is preferable that the solution contain no more than a minor amount of water and therefore it seems desirable to have the water content as low as possible. For good yields we desire to concentrate and remove the precipitated sodium sulphate by filtration as set forth in the examples, or by centrifuging.

Our process is applicable to the extraction of hydracrylic acid from salts other than sodium sulphate. Thus, for example, any salt of hydracrylic acid may be converted into the free acid by reaction with any acid stronger than hydracrylic acid, e.g. sulphuric acid, hydrochloric acid, phosphoric acid, as well as organic acids stronger than hydracrylic acid such as the chloroacetic acids (mono-, di-, and tri-), maleic acid, or oxalic acid. The hydracrylic acid thus obtained will be ad-

mixed with a salt of the acid used.

Among the salts from which hydracrylic acid may be extracted we mention by way of example sodium hydracrylate, potassium hydracrylate, calcium hydracrylate, barium hydracrylate, magnesium hydracrylate, ferric hydracrylate, silver hydracrylate and lead hydracrylate.

The ketones suitable for use in accordance with our invention are acetone, methyl ethyl ketone, the methyl *n*-propyl ketone, methyl isopropyl ketone, the methyl butyl ketones and diethyl ketone. We prefer to employ the ketones boiling below about 100° C.

The proportion of extracting ketone to the hydracrylic acid may vary widely. In general from about 1 to 5 times the quantity of ketone as compared to the hydracrylic acid is suitable.

The solvent extraction process may be carried out at room temperatures or, if desired, at elevated temperatures.

Our process of converting ethylene cyanohydrin into a salt of hydracrylic acid is disclosed and claimed in our copending application for Patent No. 15933/43 and our process of producing free hydracrylic acid is described and claimed in our copending application for Patent No. 15932/43.

Obviously many modifications and variations may be made in our process without departing from the scope of the invention as defined in the appended claims.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process which comprises extracting hydracrylic acid from a mixture with a salt by means of a ketone having not more than six carbon atoms.

2. A process as in claim 1 wherein the boiling point of the ketone is below about 100° C.

3. The process which comprises extracting hydracrylic acid from a mixture with a salt by means of acetone.

4. A process which comprises extracting hydracrylic acid from sodium sulphate by means of acetone.

5. A process which comprises extracting hydracrylic acid from a salt by means of a ketone having a boiling point below about 100° C., said salt and the hydracrylic acid having been obtained by the alkaline hydrolysis of ethylene cyanohydrin followed by the liberation of hydracrylic acid by means of an acid stronger than hydracrylic acid.

Dated this 14th day of December, 1943.

CRUIKSHANK & FAIRWEATHER,
29, Southampton Buildings,
Chancery Lane, London, W.C.2,
and
29, St. Vincent Place, Glasgow,
Agents for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1945. Published at
The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies,
price 1s. 0d. each (inland) 1s. 1d. (abroad) may be obtained.